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Viscosity and diffusion co-efficient of square-well liquids

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Using Collins & Raefel's equation for transport co-efficients, the friction co-efficient, self-diffusion co-efficient and shear viscosity have been calculated with a square-well potential. A method has been developed in the evaluation of $g'(\sigma)$ and $g'(\lambda\sigma)$, the values of the space-derivatives of the R.D.F. at $r = \sigma$ and $r = \lambda\sigma$ respectively (here λ is the width of the square-well) from the structure of liquids. The present treatment gives a good agreement with the experimental data.

1. Introduction

Collins & Raefel (1958) from hydrodynamical considerations derived the friction co-efficient γ^2 as,

$$\gamma^2 = \frac{\rho}{3m} \int \nabla^2 u(r) g(r) \boldsymbol{dr}. \qquad \ldots (1)$$

Here, $\rho = N/V$, m is the mass of a molecule, $u(r)$ is the interaction potential and $g(r)$ is the well-known radial distribution function (R.D.F.) and $\boldsymbol{dr}$ is the volume element at $\boldsymbol{r}$. They also derived the following equation for shear viscosity μ of liquid,

$$\mu^2 = \frac{m \times \rho^{7/3}}{7{\cdot}848 \times 15} \int_0^\infty \left[r^2 \frac{\partial^2 u}{\partial r^2} + 9r \frac{\partial u}{\partial r} \right] g(r) \boldsymbol{dr}. \qquad \ldots (2)$$

We use here the square-well potential as the interaction potential $u(r)$, which has both hard part as well as some softness. It may, thus, be regarded as perturbation on the rigid-sphere potential and, as such, is less hypothetical than the rigid-sphere potential.

2. Calculation and Results

The square-well potential can be represented as,

$$\begin{aligned} u(r) &= \infty, && r < \sigma \\ &= -\epsilon, && \sigma < r < \lambda\sigma \\ &= 0, && r \nleq \lambda\sigma \end{aligned}$$

where, ϵ is defined as the depth of the square-well; n, the width. The gradient of potential $\partial u/\partial r$ is given by (Reed & Gubbins 1973),

$$\begin{aligned} \frac{\partial u}{\partial r} &= -\infty, && r = \sigma \\ &= \infty, && r = \lambda\sigma \\ &= 0, && r \neq \sigma, \lambda\sigma. \end{aligned}$$

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Thus, $\partial u/\partial r$, can be represented by a suitable δ-function in the defined domains as,

$$\frac{\partial u}{\partial r} = -kT\,\delta(r-\sigma), \qquad \text{for } r = 0 \text{ to } \sigma^+ \qquad \ldots (3)$$

$$= -kT(1-e^{\varepsilon/kT})\delta(r-\lambda\sigma), \text{ for } r = \sigma^+ \text{ to } \infty. \qquad \ldots (4)$$

Concept of effective mass

In case of dense fluids like liquids, each molecule can be thought of as being surrounded by other molecules, the effect being simply to increase the mass of the diffusing molecule. This is referred to as *caging*. The molecule has to overcome this *caging* and the surrounding molecules have to rearrange themselves over a length l^* called correlation length so as to accommodate the diffusing molecule. The effective mass of a molecule can be calculated by assuming it to be a sphere of diameter l^* and is given by (Egelstaff 1967),

$$m^* = \frac{m\pi l^{*3}\rho^*}{6} \qquad \ldots (5)$$

Here, ρ^* is the actual number density at $r = \sigma$, because the cage effect is solely due to the immediate neighbours. We, therefore, can immediately write,

$$m^* = m\eta g(\sigma)\left(\frac{l^*}{\sigma}\right)^3 \qquad \ldots (6)$$

where, $\eta = \pi\rho\sigma^3/6$ is the packing, fraction, $g(\sigma)$ is the value of $g(r)$ at $r = \sigma$, which is that of a rigid sphere. Since the cage effect is due to immediate neighbours, we conclude that the rigid sphere domain only contributes to the effective mass.

This concept of effective mass enables us to rewrite eqs. (1) and (2) as,

$$\gamma^2 = \frac{\rho}{3m^*}\int \nabla^2 u(r)g(r)\boldsymbol{dr} \qquad \ldots (7)$$

and

$$\mu^2 = \frac{m^* \times \rho^{7/3}}{7{\cdot}848 \times 15}\int_0^\infty \left[r^2\frac{\partial^2 u}{\partial r^2} + 9r\frac{\partial u}{\partial r}\right]g(r)\boldsymbol{dr} \qquad \ldots (8)$$

Derivation of an expression for friction constant γ in terms of space-derivative of $g(r)$:

From eq. (7), we have,

$$\gamma^2 = \frac{4\pi\rho}{3m_*}\int_0^\infty \left(r^2\frac{\partial^2 u}{\partial r^2} + 2r\frac{\partial u}{\partial r}\right)g(r)dr. \qquad \ldots (9)$$

From eq. (9) and using the properties of Dirac δ-function (Morse & Feshbach 1953), we immediately get,

$$\gamma^2 = \frac{4\pi\rho}{3m^*}\left[-kT\int_0^{\sigma} r^2 g(r)\delta'(r-\sigma)dr-(1-e^{\varepsilon/kT})kT\int_0^{\lambda\sigma} r^2 g(r)\delta'(r-\lambda\sigma)dr\right.$$

$$\left.-2kT\int_0^{\sigma} rg(r)\delta(r-\sigma)dr-2kT(1-e^{\varepsilon/kT})\int_{\sigma}^{\lambda\sigma} rg(r)\delta(r-\sigma)dr\right]$$

$$=\frac{4\pi\rho kT\sigma^2}{3m^*}[g'(\sigma)+(1-e^{\varepsilon/kT})\lambda^2 g'(\lambda\sigma)]. \quad \ldots \quad (10)$$

Eq. (10) is important because the friction constant is related to molecular diameter σ, a microscopic parameter and space-derivative of $g(r)$ at $r=\sigma$ and $r=\lambda\sigma$.

As is well known (Egelstaff 1967), the friction constant γ is related to the diffusion co-efficient D by the equation,

$$D=\frac{kT}{m^*\gamma} \quad \ldots \quad (11)$$

Evaluation of Shear Viscosity

The integral I in eq. (8) can be written as,

$$I=4\pi\int_0^{\infty}\left(r^4\frac{\partial^2 u}{\partial r^2}+9r^3\frac{\partial u}{\partial r}\right)g(r)dr. \quad \ldots \quad (12)$$

In an exactly similar way as that in friction co-efficient, this integral can be written as,

$$I=4\pi\sigma^3 kT[\sigma\{g'(\sigma)+(1-e^{\varepsilon/kT})\lambda^4 g'(\lambda\sigma)-5\{g(\sigma)+(1-e^{\varepsilon/kT})\lambda^3 g(\lambda\sigma)\}] \quad \ldots \quad (13)$$

Hence the viscosity of a liquid can be written as :

$$\mu^2=\frac{4\pi m^* kT\sigma^3\rho^{7/3}}{7\cdot 848\times 15}[\sigma\{g'(\sigma)+(1-e^{\varepsilon/kT})\lambda^4 g'(\lambda\sigma)\}-5\{g(\sigma)+(1-e^{\varepsilon/kT})\lambda^5 g(\lambda\sigma)\}] \quad (14)$$

So the evaluation of transport co-efficients depends mainly on the computation of $g(\sigma)$, $g'(\sigma)$ and $g'(\lambda\sigma)$, the first quantity refers to the value of $g(r)$ at $r=\sigma$ and the latter two refer to the space-derivatives of $g(r)$ at $r=\sigma$ and $r=\lambda\sigma$. We will now give in detail the determination of $g(\sigma)$ and the space-derivatives of $g(r)$

Evaluation of $g'(r)$

It is well-known (March 1968) that the total correlation function $h(r)$ can be expressed in terms of the structure factor $S(k)$ as,

$$h(r)\equiv g(r)-1$$

$$=\frac{1}{2\pi^2\rho}\int[S(k)-1]\frac{k\sin kr}{r}dK. \quad \ldots \quad (15)$$

Here k is the wave-vector in the reciprocal space and is given by,

$$k=\frac{4\pi\sin 2\theta}{\lambda_t} \quad \ldots \quad (16)$$

where, λ_i is the wavelength of the incident radiation and 2θ is the scattering angle $g(\sigma)$ can be directly calculated from eq. (15) at $r = \sigma$. Further from eq. (15), we get (differentiating under integral sign),

$$g'(r) = -\frac{h(\sigma)}{\sigma} + \frac{1}{2\pi^2\rho}\int [S(k)-1]\frac{k^2\cos kr}{r}\,dK. \tag{17}$$

Therefore,

$$g'(\sigma) = -\frac{h(\sigma)}{\sigma} + \frac{1}{2\pi^2\rho\sigma}\int [S(k)-1]k^2\cos k\sigma\,dK \tag{18}$$

and,

$$g'(\lambda\sigma) = -\frac{h(\lambda\sigma)}{\lambda\sigma} + \frac{1}{2\pi^2\rho\lambda\sigma}\int [S(s)-1]k^2\cos k\lambda\sigma\,dK. \tag{19}$$

Again,

$$S(k) = \frac{}{1-\rho\tilde{C}(k)} \tag{20}$$

where $\tilde{C}(k)$ is the Fourier Transform (F.T.) of the direct correlation function (D.C.F.) $C(r)$. The F.T. $\tilde{C}(k)$ is computed for square-well given already in several papers (viz., Gopala Rao & Murthy 1974, Gopala Rao & Nammalvar 1975) and hence, the value of $S(k)$. This value of $S(k)$ is used in the computation of $g'(\sigma)$ and $g'(\lambda\sigma)$ in eqs. (18) and (19) using standard values of σ, c/k and n (Hirschfelder *et al* 1954, Gopala Rao & Murthy 1975). When once $g'(\sigma)$ and $g'(\lambda\sigma)$ are evaluated, it becomes easy to calculate the friction co-efficient, diffusion co-efficient and the shear viscosity from eqs. (10), (11) and (14) respectively.

3. Discussion of the Results

The values of friction constant and diffusion co-efficient are given in Table 1, while the values of viscosity are given in Table 2 for some typical insulating

Table 1. Self Diffusion coefficient

	Liquids	T°K	σ A	$V_{c\text{-}c}$.	$\gamma(\times 10^{12})$	$D = \frac{kT}{m^*\gamma}$ cm^2sec^{-1} present	D_{expt}
Non-ionic Liquids	Argon	84·4	3·16	28·0	1·935	$1{\cdot}23\times10^{-5}$	1·60
	Ne	25	2·38	16·3	1·11	1·50 ,,	—
	Kr	120	3·36	34·7	1·31	1·40 ,,	1·70
	Xe	163	3·76	43·0	1·15	1·20 ,,	1·30
Metallic Liquids	Na	387	3·306	25·0	4·11	3·14 ,,	4·60
	K	338	4·107	47·0	2·96	2·7 ,,	4·01
	Rb	313	4·306	55·5	1·54	1·6 ,,	2·60
	Cs	303	4·808	74·0	1·27	1·19 ,,	—
	Hg	238	2·80	14·8	1·169	0·75 ,,	0·93
	Al	943	2·45	11·3	3·30	3·39 ,,	—

Table 2

Liquids	T°K	ϵ/K°	σ A	λ	$V_{c\cdot c\cdot}$	$g(\sigma)$	$g'(\sigma) \times 10^6$	$g(\lambda\sigma)$	$g'(\lambda\sigma) \times 10^6$	μ present (Poise)	μ expt. (Poise)
Ar	84·4	64·40	3·160	1·85	28·0	1·035	9·898	0·8367	−1·7730	$2{\cdot}67 \times 10^{-3}$	$2{\cdot}70 \times 10^{-3}$
Ne	25	19·50	2·382	1·87	16·3	0·529	7·662	0·7498	−1·8820	$1{\cdot}18 \times 10^{-3}$	—
Kr	120	98·30	3·360	1·85	34·7	1·070	10·050	0·8500	−2·1580	$5{\cdot}00 \times 10^{-3}$	$3{\cdot}78 \times 10^{-3}$
Xe	163	127·00	3·760	1·85	43·0	1·320	10·950	0·8619	−1·7850	$7{\cdot}30 \times 10^{-3}$	$5{\cdot}50 \times 10^{-3}$
Na	387	111·60	3·306	1·65	25·0	1·950	11·550	0·7084	−0·3943	$0{\cdot}724 \times 10^{-2}$	$0{\cdot}68 \times 10^{-2}$
K	338	96·14	4·107	1·65	47·0	1·950	12·130	0·6892	−0·1199	$0{\cdot}60 \times 10^{-2}$	$0{\cdot}51 \times 10^{-2}$
Rb	313	96·14	4·306	1·65	55·5	1·900	11·770	0·7004	−0·5190	$0{\cdot}95 \times 10^{-2}$	$0{\cdot}71 \times 10^{-2}$
Hg	238	100·00	2·800	1·73	14·8	1·881	11·310	0·8339	−0·1144	$2{\cdot}20 \times 10^{-2}$	$1{\cdot}96 \times 10^{-2}$
Al	943	160·00	2·450	1·30	11·3	1·630	8·870	1·1100	−1·0860	$1{\cdot}13 \times 10^{-2}$	—
Cs	303	109·50	4·808	1·70	74·0	2·026	13·170	0·8190	−0·6086	$1{\cdot}08 \times 10^{-2}$	$0{\cdot}70 \times 10^{-2}$

and metallic liquids. The experimental values of diffusion co-efficient and viscosity (Cini Castagnoli 1964, Gopala Rao 1975, Johnson *et al* 1956, Naghizadeh *et al* 1962, Prigogine 1973) are also tabulated side by side with our calculated values for comparison. The agreement is surprisingly striking with this simple treatment involving analytical expressions for transport co-efficients. It is important to note here that the transport co-efficients have been calculated from the potential parameters and R.D.F. only and no arbitrary factors enter into their calculations. Further it appears from the calculated results that metallic liquids conform to the square-well potential, Similar conclusions have also been very recently arrived at (Gopala Rao & Murthy 1975).

References

Cini Castagnoli 1964 *Physica* **30**, 953.

Collino C. K. & Raefel H. J. 1958 *J. Chem. Phys.* **29**, 699.

Egelstaff P. A. 1967 *An Introduction to Liquid State*, Academic Press, p. 158; *ibid.* p. 127.

Gopala Rao R. V. & Nammalvar T. 1975 *Chem. Phys. Lett.* **31**, 113.

Gopala Rao R. V. & Murthy A. K. 1974 *Phys. Stat. Sol.* (b) **66**, 703.

Gopala Rao R. V. & Murthy A. K. 1975 *Zeit. Naturforsch.* **30**, 619.

Gopala Rao R. V. 1975 *Ind. J. Pure App. Phys.* **13**, 459.

Hirschfelder J. O., Curtiss C. F. & Bird R. B 1954 *Molecular theory of gases and liquids*, John Wiley & Sons, p. 160.

Johnson P. A. & Babb A. L. 1956 *Chem. Rev.* **56**, 387.

March N. H. 1968 *Liquid Metals*, Pergamon Press, p. 7.

Morse P. M. & Feshbach H. 1953 *Methods of Theoretical Physics* Part I, McGraw-Hill Book Co., p. 837.

Naghizadeh J. & Rice S. A. 1962 *J. Chem. Phys.* **36**, 2710.

Prigogine I. & Rice S. A. 1973 *Advances in Chemical Physics*, John Wiley & Sons, Vol. XXIV, p. 270.

Reed T. M. & Gubbins K. E. 1973 *Applied Statistical Mechanics*, McGraw-Hill Book Co., p. 469.